

BIODIESEL AS A POTENTIAL RENEWABLE ENERGY RESOURCE: A REVIEW

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ABSTRACT

Today not only the transport but also all the human activities are highly energy intensive. For which we are almost totally dependent on fossil fuels. The scarcity of conventional fossil fuels, growing emissions of pollutants during combustion, and their increasing costs brought in to focus the need for developing alternate fuels for the survival of the mankind. An alternative fuel to petrodiesel must be technically feasible, economically competitive, environmentally acceptable, and easily available. Biomass among all alternative fuels has been proved to more attractive and promising energy resource as just one by eighth of total biomass produced annually worldwide can fulfill all of humanity's current demand. Moreover, the huge potential of biomass is yet to be explored as its abundance on the globe is highest among all renewable resources. Various techniques are available for the conversion of biomass into biofuels such as bioethanol and biodiesel and thermochemical conversion products. The commercialization and development of biofuels is dependent upon various parameters for the advancement of this technology. The present article investigates and summarizes different aspects of biodiesel energy resource such as types of sources, methods of synthesis and their physical and chemical properties.

KEYWORDS: Biodiesel, Renewable Energy Resource, Transestrification, Triglyceride

INTRODUCTION

Alternative fuels for diesel engines are becoming increasingly important due to the diminishing petroleum reserves. The supply of petroleum fuels strongly depends on a small number of oil exporting countries. Therefore there is increasing trend in the prices of the crude oil¹. India imported 75% of its crude oil requirements from other countries to meet the energy needs, which will increase to 90% by 2020. It has been estimated that the demand for diesel will be 66.90 MMT for the year 2011-2012². The growing environmental concerns have made renewable fuels an exceptionally attractive alternative as a fuel for the future. To meet the rising energy demand and replace reducing petroleum reserves, fuels such as biodiesel and bioethanol are in the forefront of alternative technologies³. Biomass is a carbon-neutral source⁴.

Biodiesel is derived from a wide range of edible and non-edible vegetable oils, animal fats, used frying oils and waste cooking oils through various methods. Biodiesel is now mainly being produced from rapeseed, soybean, and palm oils. These oils are too viscous to be used as a fuel in compression-ignition engines on the other hand, biodiesel exhibits great potential for CI engines. It can be prepared by various methods. Transesterification is a common method of biodiesel production in which chemical reaction between triglyceride and alcohol in the presence of catalyst or without catalyst take place. Transesterification is widely used to reduce vegetable oil viscosity⁵.

What is Biodiesel?

Biodiesel (Greek, bio= life, diesel from Rudolf Diesel) refers to a diesel-equivalent, processed fuel derived from

biological sources. It is a mixture of methyl esters of long-chain fatty acids like lauric, palmitic, stearic, oleic, *etc.* and is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst or without catalyst to yield methyl or ethyl esters (biodiesel) and glycerine⁶. Generally, methanol being less expensive than ethanol is preferred for transesterification. In technical terms (ASTM D 6751) biodiesel is a diesel engine fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100 and meeting the requirements of ASTM D 6751. Various technical properties of biodiesel is given in Table 1. Pure biodiesel is referred as B100 while biodiesel blends are referred as BXX. The XX indicates the amount of biodiesel in the blend (*i.e.*, a B80 blend is 80% biodiesel and 20% petrodiesel).

Sources for Biodiesel Production

There are various biodiesel sources which may be edible or non-edible such as almond, andiroba (*Carapa guianensis*), babassu (*Orbignia sp.*), barley, camelina (*Camelina sativa*), coconut, copra, cumaru (*Dipteryx odorata*), *Cynara cardunculus*, fish oil, groundnut, *Jatropha curcas*, karanja (*Pongamia glabra*), laurel, *Lesquerella fendleri*, *Madhuca indica*, microalgae (*Chlorella vulgaris*), oat, piqui (*Caryocar sp.*), poppy seed, rice, rubber seed, sesame, sorghum, tobacco seed, and wheat⁵. A variety of bio-lipids can also be used to produce biodiesel such as animal fats including tallow, lard *etc.*

In USA soybean, in Malaysia and Indonesia, palm oil and in Europe, rapeseed oil is the primary source for biodiesel production. In India and Southeast Asia, the jatropha tree is used as a significant fuel source. Algae can grow anywhere in presence of enough sunshine and even in saline water. The yield of algal oil is highest among all the biodiesel resources. According to some estimates, the yield (per acre) of oil from algae is over 200 times the yield from the best performing plant/vegetable oils⁷. Approximately 46 tons of oil/hectare/year can be produced from diatom algae.

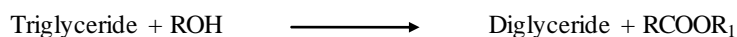
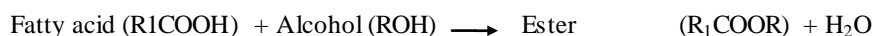
Methods of Synthesis of Biodiesel

Vegetable oil has very high viscosity for use in most existing diesel engines as a straight replacement fuel oil. However, to reduce the viscosity of vegetable oils different techniques can be adopted, such as dilution, micro-emulsification, pyrolysis, and transesterification. One of the most common methods used to reduce oil viscosity in the biodiesel industry is called transesterification. Transesterification Methods can be catalytic (catalyzed by acid, alkali, diazomethane (CH_2N_2)) and supercritical alcohol transesterification (non-catalytic, catalytic and biocatalytic).

Chemical conversion of the oil into its corresponding fatty ester is called transesterification⁸. Transesterification (also called alcoholysis) is the reaction of a fat or oil triglyceride with an alcohol to form monoesters and glycerol (Figure 1). A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. The purpose of the transesterification process is to lower the viscosity of oil. The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) or heterogeneous catalysts such as metal oxides or carbonates. Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield⁹.

Bases can catalyze the reaction by removing a proton from the alcohol, while acids can catalyze the reaction by donating a proton to the carbonyl group, thus making it more reactive¹⁰. The parameters affecting the methyl ester formation are reaction temperature, pressure, molar ratio, water content, and free fatty acid content. It was observed that

increasing the reaction temperature had a favorable influence on the yield of ester conversion. The yield of alkyl ester increased when the oil-to alcohol molar ratio was increased⁶.



The formation of alkyl esters from monoglycerides may be the rate determining step since monoglycerides are the most stable intermediate compound¹¹.

Thermal Degradation of Fatty Acids during Biodiesel Production

The higher the unsaturation in a fatty oil or ester, the more susceptible it will be for oxidation. When a diene is converted into conjugated diene by spontaneous rearrangement, it reacts with molecular oxygen and form a lipid peroxy radical. This produces a lipid hydroperoxide (LOOH) by the abstraction of a proton from neighboring polyunsaturated fatty acids and regenerate a carbon-centered lipid radical which propagates the radical reaction¹².

After hydrogen is removed from such carbons oxygen rapidly attacks and a LOOH is formed again and again. This reaction is a chain mechanism that can proceed rapidly once an initial induction period has occurred (Figure 2). LOOHs thus formed, decompose and interact with each other and form numerous secondary oxidation products including higher molecular-weight oligomers.

Recovery of Glycerine

Triglycerides are readily transesterified in the presence of catalyst at atmospheric pressure and at a temperature of approximately 60 to 70°C. The mixture at the end of reaction is allowed to settle. It produces two liquid phases: ester and crude glycerol. The heavier layer of glycerol is left on the bottom and the methyl ester (biodiesel) is on the top after several hours. After settling is complete the lower glycerol layer is drained and the upper ester layer remains⁸. The upper methyl ester layer is washed by adding water at the rate of 5.0% by volume of the oil and then stirred for 5 min and then glycerol allowed to settle again. The recovery of high-quality glycerol as a biodiesel byproduct is a primary action to be considered to lower the cost of biodiesel. The glycerin can be used to make soap (or any one of 1,600 other products). The excess methanol is recovered by distillation and sent to a rectifying column for purification and recycled¹³.

Fuel Properties of Biodiesel

Viscosity, Density and Flash Point

Viscosity is the most important property of biodiesel since at low temperatures it affects the fluidity of the fuel which affects the operation of fuel injection equipment. Poorer atomization of the fuel spray and less accurate operation of the fuel injectors is due to the high viscosity of fuel. The lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets¹⁴. The molecular weight of biodiesel remains one third to that of the triglycerides and viscosity reduces by a factor of about eight after its formation by transesterification. Biodiesels have a viscosity close to that of diesel fuels (Table 2).

The viscosity values of vegetable oils are between 27.2 and 53.6 mm²/s, whereas those of vegetable oil methyl esters are between 3.6 and 4.6 mm²/s. Compared to D₂ fuel, all of the vegetable oil methyl esters are slightly viscous as viscosity values of D₂ fuel is 2.7*10⁻⁶ m²/s at 311 K¹⁵ while the flash point values of vegetable oil methyl esters are much lower than those of vegetable oils. An increase in density from 860 to 885 kg/m³ for vegetable oil methyl esters increases the viscosity from 3.59*10⁻⁶ to 4.63*10⁻⁶ m²/s, and the increases are highly regular. There is high regression between the density and viscosity values of vegetable oil methyl esters.

$$D = 33.107V + 745.39$$

Where D is the density and V is the viscosity of a biodiesel sample. There is high regression between the viscosity and density values of biodiesel samples ($R^2 = 0.9093$). The relationships between viscosity and flash point for vegetable oil methyl esters are irregular.

$$F = 32.641V + 305.02$$

Where F is the flash point and V the viscosity of a biodiesel sample. There is high regression between viscosity and density values of biodiesel samples ($R^2 = 0.9357$).

$$F = 0.9323D - 282.64$$

Where F is the flash point and D the density of a biodiesel sample. There is high regression between the viscosity and density values of biodiesel samples ($R^2 = 0.8753$). There are high regressions between the density, viscosity, and flash point values of vegetable oil methyl esters¹⁶.

Cetane Number, Cloud Point and Pour Point

The cetane number is a measure of the ignition quality of diesel fuels, and a high CN implies short ignition delay. It is based on two compounds, hexadecane (CN = 100) and heptamethylnonane (CN = 15). The CN of biodiesel is generally higher than conventional diesel. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN. The CP is the temperature at which wax first becomes visible when the fuel is cooled. The PP is the temperature at which the amount of wax from a solution is sufficient to gel the fuel; thus it is the lowest temperature at which the fuel can flow. Biodiesel has a higher CP and PP compared to conventional diesel¹⁷.

Higher Heating Values of Biodiesel

The structural oxygen content of a fuel improves its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. Biodiesel contains 11% oxygen by weight and no sulfur. Because of this the combustion efficiency of biodiesel is higher than that of petrodiesel. The HHVs of biodiesels (39 to 41 MJ/kg) is slightly lower than that of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg), or petroleum (42 MJ/kg), but higher than coal (32 to 37 MJ/kg) (Table 3).

Water Content

The presence of water content has a negative effect on the yield of biodiesel hence the feedstock should be free from water. Even a small amount of water (0.1%) in the transesterification reaction causes soap formation which consumes catalyst and thus reduces the effectiveness of catalyst¹⁸ also reported a precautionary step to prevent moisture absorbance and maintenance of catalytic activity by preparing the fresh solution of potassium hydroxide and methanol.

The presence of water had negligible effect on the conversion while using lipase as a catalyst¹⁹

The soap can prevent the separation of biodiesel from glycerol fraction²⁰. In catalyzed methods, the presence of water has negative effects on the yields of methyl esters. However, the presence of water positively affects the formation of methyl esters in the supercritical methanol method²¹.

Emissions from Biodiesel

Many studies on the performances and emissions of compression ignition engines, fuelled with pure biodiesel and blends with diesel oil, have been conducted and are reported in the literature^{22,23}. Biodiesel has demonstrated a number of promising characteristics, including reduction of exhaust emissions²⁴. The combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons, 75-90% reduction in polycyclic aromatic hydrocarbons and a significant reductions in particulate matter and carbon monoxide than petroleum diesel fuel. However, biodiesel provides a slight increase or decrease in nitrogen oxides depending on the type of engine and testing procedures. Biodiesel contains little nitrogen, as compared with petrodiesel, which is also used as a reburning fuel.

Biodiesel contains trace amounts of sulfur, therefore, SO₂ emissions are reduced in direct proportion to the petrodiesel replacement. For B20 soybean-based biodiesel, the estimated emissions for percent change in emissions of NO_x, PM, HC, and CO were +20%, -10.1%, -21.1%, and -11.0%, respectively²⁵. The blends of biodiesel and diesel oil are preferred in engines so as to avoid problems related to the decrease of power and torque and to the increase of NO_x emissions which is due to increase of biodiesel content in the blend²⁶. Figure 3 shows the average emission impacts of vegetable-oil-based biodiesel for CIEs. Carbon dioxide emissions are reduced about 77 -104 g/MJ of diesel displaced by biodiesel. These reductions increase as the amount of biodiesel blended into the diesel fuel increases.

The basic emission correlation equations and related correlation coefficients from Figure 3 are as follows:

$$\text{For NO}_x \ Y = 0.1078X - 0.0272 \ (r^2 = 0.9954)$$

$$\text{For PM} \ Y = -0.4673X - 2.2182 \ (r^2 = 0.9894)$$

$$\text{For CO} \ Y = -0.4695X - 2.5591 \ (r^2 = 0.9886)$$

$$\text{For HC} \ Y = -0.6715X - 5.3273 \ (r^2 = 0.9761)$$

Biodegradability of Biodiesel

Biodiesel is non-toxic and eco-friendly as it degrades biologically through enzymatic action. It degrades about four times faster than petrodiesel due to oxygen content present in its structure. As biodiesel fuels are becoming commercialized, their existence in the environment is an area of concern since petroleum oil spills constitute a major source of contamination of the ecosystem. Biodiesel is highly biodegradable in freshwater in case they enter the aquatic environment in the course of their use or disposal. About 90–98% of biodiesel is mineralized in 21–28 days under aerobic as well as anaerobic conditions²⁷. In one study, after 28 d all biodiesel fuels were 77 to 89% biodegraded; diesel fuel was only 18% biodegraded²⁸. The enzymes responsible for the dehydrogenation/oxidation reactions attack oxygen atoms immediately²⁹. In 28 days heavy fuel oil biodegrade about 11%³⁰, gasoline about 28% and vegetables oils and their derived methyl esters (biodiesels) degrade rapidly about 76-90%²⁹.

Disadvantages of Biodiesel as Diesel Fuel

The major challenges for the commercialization of biodiesel are their higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NO_x) emissions, lower engine speed and power, injector coking, engine compatibility, high price, and higher engine wear. The power is decreased on an average 5% by using biodiesel. In place of diesel at rated loads³¹. The operating disadvantages of biodiesel in comparison with petrodiesel are cold start problems, lower energy content, higher copper strip corrosion, and fuel pumping difficulty due to high viscosity which increases fuel consumption. The high value of vegetable oil as a food product makes the production of a cost-effective fuel very challenging. However, there are large amounts of low-cost oils and fats, such as restaurant waste and animal fats that could be converted into biodiesel. The problem with processing these low cost oils and fats is that they often contain large amounts of free fatty acids that cannot be converted into biodiesel using an alkaline catalyst³².

CONCLUSIONS

Biodiesel has significant potential for use as an alternative fuel in compression ignition engines. Biodiesel is a plant-derived product and contains oxygen in its molecules, making it a cleaner-burning fuel than petrol and diesel. It is non-flammable and, in contrast to petrodiesel, is non-explosive, with a flash point of 423 K for biodiesel as compared to 337 K for petrodiesel. Unlike petrodiesel, biodiesel is biodegradable and non-toxic, and it significantly reduces toxic and other emissions when burned as a fuel. It is free of sulfur and carcinogenic compounds. Currently, biodiesel is more expensive to produce than petrodiesel, which appears to be the primary factor in preventing its more widespread use and current worldwide production of vegetable oil and animal fat is not enough to replace liquid fossil fuel use (maximum replacement percentage: *ca.* 20 to 25%). The advantages of biodiesel as diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, and lower sulfur and aromatic content, higher cetane number, and higher biodegradability. The main advantages of biodiesel given in the literature include its domestic origin, which would help reduce a country's dependency on imported petroleum, its biodegradability, high flash point, and inherent lubricity in the neat form.

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APPENDICES

Table 1: Technical Properties of Biodiesel

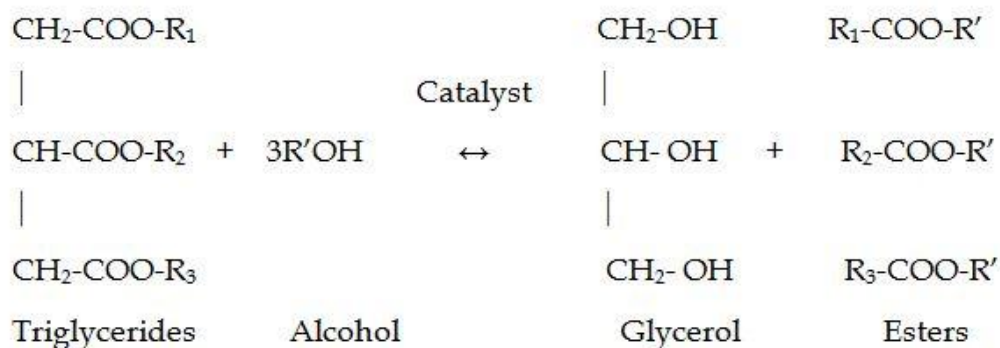
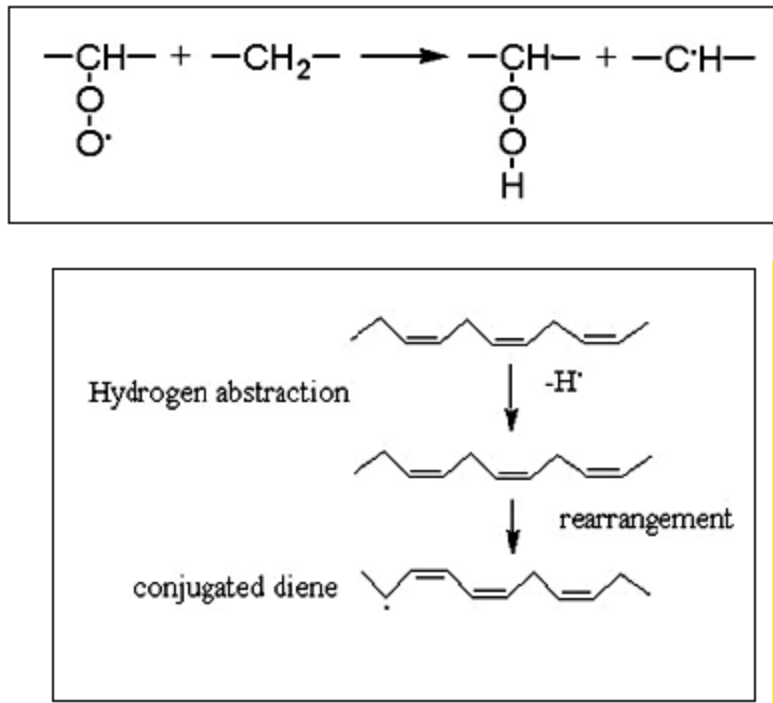
Common Name	Biodiesel
Common chemical name	Fatty acid methyl/ethyl ester
Chemical formula range	C ₁₄ –C ₂₄ methyl esters or C ₁₅ – ₂₅ H ₂₈ – ₄₈ O ₂
Kinematic viscosity range (mm ² /s, at 313 K)	3.3–5.2
Density range (kg/m ³ , at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	430–455
Distillation range (K)	470–600
Solubility in water	Insoluble
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel

Table 2: Viscosity, Density and Flash Point Measurements of Nine Oil Methyl Esters

Methylesters	Viscosity mm ² /s (at 313 K)	Density kg/m ³ (at 288 K)	Flash Point K
Cottonseed oil	3.75	870	433
Linseed oil	3.4	887	447
Mustard oil	4.1	885	441
Palm oil	3.94	880	431
Rapeseed oil	4.6	894	453
Soybean oil	4.08	885	441
Sunflower oil	4.16	880	439

Table 3: Comparison of Chemical Properties and Higher Heating Values (HHVs) between Biodiesel and D₂ Fuels

Chemical Property	Biodiesel (Methylester)	D ₂ Fuel
Ash (wt.%)	0.002–0.036	0.006–0.010
Sulfur (wt.%)	0.006–0.020	0.020–0.050
Nitrogen (wt.%)	0.002–0.007	0.0001–0.003
Aromatics (vol.%)	0	28–38
Iodine number	65–156	0
HHV (MJ/kg)	39.2–40.6	45.1–45.6

**Figure 1: Transesterification of Triglycerides with Alcohol****Figure 2: Mechanism of Peroxy Radical Formation on Methylene Group**

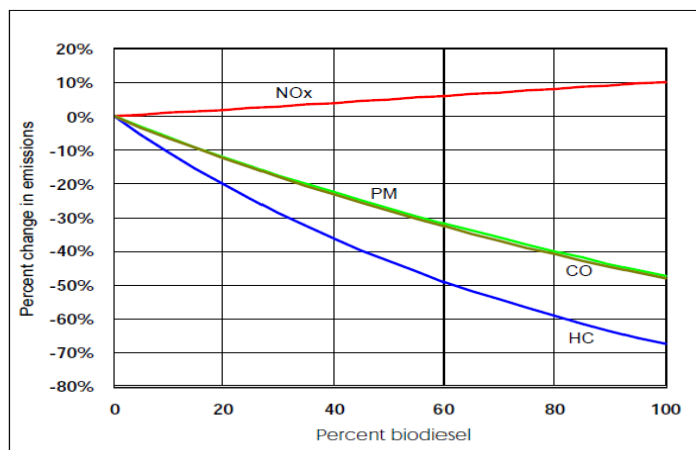


Figure 3: Average Emission Impacts of Vegetable-Oil-Based Biodiesel for CIEs